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OPTICAL CATALYST TILE AND METHOD OF MANUFACTURE THEREOF

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Specification

1. Title of the invention

Optical Catalyst Tile and Method of Manufacture Thereof

2. Claims /2

1. An optical catalyst tile, characterized by the fact that in an optical catalyst tile in which a coated film having an optical catalyst function is formed on the surface, the thickness of said coated film is thicker than 0.8 μm.

2. The optical catalyst tile of Claim 1, characterized by the fact that the coated film is substantially composed of only TiO_2.

3. The optical catalyst tile of Claim 1 or 2, characterized by the fact that the coated film covers the entire surface of the tile surface.

4. A method for manufacturing an optical catalyst tile, characterized by the fact that a tile is heated in a heating zone; and TiO_2 generated by the hydrolysis of $TiCl_4$ vapor is vapor-deposited on said tile surface in a vapor deposition chamber into which said $TiCl_4$ vapor generated by a $TiCl_4$ vapor generating furnace is introduced, so that a coated film containing a crystalline TiO_2 with a thickness of greater than 0.8 μm is formed on the tile surface.

5. The method for manufacturing an optical catalyst tile of Claim 4, characterized by the fact that the tile is heated at 300-800°C in the heating zone.

6. The method for manufacturing an optical catalyst tile of Claim 4, characterized by the fact that the temperature of said heating zone is set to 500-700°C; and the temperature of the $TiCl_4$ vapor generating furnace is set to 45°C or higher.

7. The method for manufacturing an optical catalyst tile of any of Claims 4-6, characterized by the fact that the TiO_2 coated film formed by the vapor deposition is further baked at 500-900°C.

3. Detailed explanation of the invention

[0001]

(Technical field of the invention)

The present invention pertains to an optical catalyst tile and its manufacturing method. In particular, the present invention pertains to an optical catalyst tile, which raises an optical catalyst effect by forming a coated film (hereinafter, sometimes called "optical catalytic coated film") having an optical catalyst function of a thick film on the tile surface and prevents an iris phenomenon due to the interference, and a method for manufacturing the optical catalyst tile by a chemical vapor deposition method (CVD).

[0002]

(Prior art)

In order to prevent the cloudiness or waterdrop formation of transparent base materials such as mirrors, lenses, and sheet glasses by making the surface of the base materials highly hydrophilic or in order to prevent the contamination of the surface and to render a self-cleaning function of the surface by making the surface of construction materials or mechanical devise or various kinds of articles highly hydrophilic, an optical

catalytic coated film such as optical catalytic titania (TiO_2) is formed on the base material surface (Japanese Kokai Patent Application No. Hei 9[1997]-241038, International Laid-Open Patent No. WO96/29375, and Japanese Kokai Patent Application No. Sho 61[1987]-83106). Substances having an optical catalyst function such as optical catalytic titania make the base material surface highly hydrophilic by the hydrophilic effect due to an optical excitation, prevent the formation of waterdrops, and prevent the cloudiness due to scattering of lights. Also, stains containing a large amount of lipophilic component are difficult to be attached, and the self-cleaning and action of the surface can be obtained, so that attached stains are also easily dropped. Also, the above-mentioned effects can be raised by the acceleration of the decomposition of NOx or SOx or organic substances through the optical catalyst effect.

[0003] The optical catalytic coated films such as TiO_2 has been formed as a thin film of 100-800 nm (Japanese Kokai Patent Application No. Hei 9[1997]-241038) or about 0.2 μm or smaller (International Laid-Open Patent No. WO96/29375). As a method for forming the film with such an optical catalyst function, a sol-gel method for spreading and baking a suspension containing TiO_2 particles is described in Japanese Kokai Patent Application No. Hei 9[1997]-241038) and International Laid-Open Patent No. WO96/29375.

[0004] In Japanese Kokai Patent Application No. Sho 61[1986]-83106, a CVD is described as a method for forming a coated film, however its film formation conditions and the coated film thickness are not particularly considered. Also, in case the TiO_2 coated film is formed on the title surface by the CVD, generally, as shown in Figure 1, a tile 2 is placed on a tile transfer belt, transferred to a heating zone 3, heated, and transferred to a vapor deposition chamber 4 into which $TiCl_4$ vapor generated by a $TiCl_4$ (titanium

tetrachloride) vapor generating furnace 5 is introduced, and TiO_2 generated by a hydrolysis reaction of the following equation in the vapor deposition chamber 4 is vapor-deposited on the title surface and cooled in a cooling zone 6, so that a film is formed.

[0005]

$TiCl_4 + 2H_2O \rightarrow TiO_2 + 4HCl$

In forming the TiO_2 coated film of the CVD, the temperature of the heating zone set to 300-500°C, the temperature of the $TiCl_4$ vapor generating furnace is se to about 35°C, and a TiO_2 coated film with a thickness of about 0.08 μm is formed.

[0006]

(Problems to be solved by the invention)

In the conventional technique for forming the optical catalytic coated film at a thickness of 800 nm (= 0.8 μm) or smaller, an iris phenomenon was easily generated by the interference of lights, and there was a problem in terms of design. Also, if the film thickness is thin, the optical catalyst effect is also inferior as much.

[0007] Also, it is difficult to form a uniform film in the film formation by using the conventional sol-gel method. According to the CVD method, a uniform film can be formed, however under the conventional CVD conditions, it is difficult to thicken the coated film.

[0008] The present invention solves the above-mentioned conventional problems, and its purpose is to provide an optical catalyst tile, which raises an optical catalyst effect by forming a thick optical catalytic coated film on the tile surface and prevents an iris phenomenon due to the interference of lights, and a method for manufacturing the optical catalyst tile by a CVD method.

[0009]

(Means to solve the problems)

The optical catalyst tile of the present invention is characterized by the fact that in an optical catalyst tile in which a coated film having an optical catalyst function is formed on the surface, the thickness of said coated film is thicker than 0.8 μm.

[0010] In the thick film in which the thickness of the optical catalytic /3 coated film is thicker than 0.8 μm, since the film thickness is thicker than the wavelength of visible lights, the iris phenomenon due to the interference is prevented. Also, since the optical catalytic coated film is thick, the optical catalyst effect is also improved, and a good contamination prevention effect can be obtained.

[0011] This coated film is preferably uniformly formed on the entire tile surface so that uncoated parts such as pinholes do not exist.

[0012] In a pattern of the present invention, the coated film is substantially composed of only TiO_2.

[0013] This optical catalyst tile of the present invention can be easily manufactured by the method of the present invention for manufacturing an optical catalyst tile characterized by the fact that a tile is heated in a heating zone; and TiO_2 generated by the hydrolysis of $TiCl_4$ vapor is vapor-deposited on said tile surface in a vapor deposition chamber into which said $TiCl_4$ vapor generated by a $TiCl_4$ vapor generating furnace is introduced, so that a coated film containing a crystalline TiO_2 with a thickness of greater than 0.8 μm is formed on the tile surface.

[0014] In this method, a coated film with a high adhesive strength can be formed by heating the tile at 300-800°C in the heating zone. Also, the optical catalytic coated film with a large film thickness can be formed by a

one-time film formation operation through setting of the temperature of the heating zone to 500-700°C and the temperature of the $TiCl_4$ vapor generating furnace to 45°C or higher.

[0015] The TiO_2 crystal phase in the coated film is further increased by baking the TiO_2 coated film formed by the vapor deposition at 500-900°C, so that the optical catalyst performance can be further raised.

[0016]

(Embodiment of the invention)

Next, an embodiment of the present invention is explained in detail.

[0017] In the present invention, as a substance having an optical catalyst function of the optical catalytic coated film being formed on the tile surface, metal oxides such as ZrO_2, ZnO, SnO_2, WO_3, Bi_2O_3, $SrTiO_3$, Fe_2O_3, and V_2O_5 are mentioned in addition to TiO_2. These metal oxides may be used alone or in combination of two kinds or more.

[0018] In a pattern of the present invention, the coated film is composed of only TiO_2. The coated film composed of only TiO_2 has a very high optical catalyst function.

[0019] In the present invention, this optical catalytic coated film is formed as a coated film thicker than 0.8 μm. If the thickness of the optical catalytic coated film is 0.8 μm or smaller, there is an iris problem due to the interference, and a sufficient optical catalyst effect cannot be obtained. If the optical catalytic coated film is excessively thick, the thickness of the optical catalytic coated film is preferably 0.8-2 μm, especially 0.8-1.2 μm.

[0020] This optical catalytic coated film can also be formed by the sol-gel method, however as mentioned above, in the sol-gel method, since the distribution of an optical catalytic substance such as TiO_2 in the optical

catalytic coated film being formed is nonuniform and a high-characteristic optical catalytic coated film with uniform properties cannot be formed, this optical catalytic coated film is preferably formed by the CVD.

[0021] Next, the method for manufacturing the optical catalyst tile of the present invention that manufactures the optical catalyst tile by forming a TiO_2 optical catalytic coated film according to the CVD is explained.

[0022] In the present invention, similarly to the conventional method shown in Figure 1 except for adopting the following appropriate CVD conditions, a CVD-TiO_2 coated film can be formed.

[0023] (1) Temperature of heating zone 3

The adhesive strength of the coated film can be raised by setting temperature of a heating zone 3 to 300-800°C. In particular, in the present invention, in order to form the TiO_2 coated film with a film thickness thicker than 0.8 μm, it is preferable to set the temperature of the heating zone 3 to 500-700°C. Thus, the TiO_2 coated film with a thick film can be formed by a one-time film formation operation through the increase of the preheating temperature of a tile 2.

[0024] (2) Temperature of $TiCl_4$ vapor generating furnace 5

In the conventional method, a temperature of the $TiCl_4$ vapor generating furnace 5 is about 35°C, however in the present invention, in order to form a TiO_2 coated film with a film thickness thicker than 0.8 m, the temperature of the $TiCl_4$ vapor generating furnace 5 is preferably set to 45°C or higher, especially 50-70°C. Thus, a large amount of $TiCl_4$ vapor is generated by raising the temperature of the $TiCl_4$ vapor generating furnace 5, so that a TiO_2 coated film with a thick film thickness can be formed. Also, in a vapor deposition chamber 4, the hydrolysis is advanced by moisture in the vapor deposition chamber, and if the humidity of the vapor deposition chamber is

low and water for the hydrolysis is deficient, a container filled with water is put into the vapor deposition chamber, and vapor is generated. Also, an air may be supplied to the vapor deposition chamber, or vapor may be added to the air.

[0025] The film thickness of the TiO_2 coated film being formed can be easily regulated by increasing and decreasing the amount of $TiCl_4$ vapor being deposited by regulating the residence time of the vapor deposition chamber 5 or regulating the temperature of the $TiCl_4$ vapor generating furnace 5.

[0026] Also, as other CVD conditions, the following conditions are preferably adopted.

[0027]

Residence time of heating zone: 15-30 min

Atmosphere of vapor deposition chamber: Air (humidification, if necessary)

Atmosphere pressure of vapor deposition chamber: Atmospheric pressure

Temperature of vapor deposition chamber: 150-250°C

Cooling rate of cooling zone: 30-40°C/min

After forming a TiO_2 vapor-deposited film by this CVD method, the TiO_2 /4 vapor-deposited film formed is preferably subjected to a crystallization annealing treatment by baking at 500-900°C. With this crystallization annealing treatment, the TiO_2 crystal phase is further increased, and the optical catalyst performance of the TiO_2 optical catalytic coated film can be raised.

[0028] Also, in forming the TiO_2 vapor-deposited film by the CVD method, a composite optical catalytic coated film such as TiO_2-SiO_2 or TiO_2-SnO_2 can be formed by combining other vapor-depositing raw materials such as $SiCl_4$ (silicon tetrachloride) and $SnCl_4$ (tin tetrachloride) along with $TiCl_4$.

[0029]

(Application examples)

Next, the present invention is explained in detail by application examples and comparative examples.

[0030] Application Examples 1-3

According to the CVD method shown in Figure 1, a TiO_2 vapor-deposited film was formed on the surface of a tile under the following CVD conditions, and the TiO_2 vapor-deposited film formed was subjected to a crystallization annealing treatment by baking at 600°C for 1 h, so that TiO_2 optical catalytic coated films with a thickness shown in Table 1 were formed. Also, the residence time of a vapor deposition chamber was set to 40 sec in Application Example 1, 60 sec in Application Example 2, and 80 sec in Application Example 3.

[0031]

Temperature of heating zone: 650°C

Residence time of heating zone 3: 15-30 min

Atmosphere of vapor deposition chamber 4: Air

Atmosphere pressure of vapor deposition chamber 4: Atmospheric pressure

Temperature of vapor deposition chamber 4: 200°C

Temperature of $TiCl_4$ vapor generating furnace 5: 65°C

Cooling rate of cooling zone: 30°C/min

For the optical catalyst tiles obtained, the existence of the iris phenomenon due to the interference was investigated with the naked eyes and evaluated by the following standards, and the results were shown in Table 1. Also, the TiO_2 coated film with a thickness of 1 μm on the average corresponds to the amount of about 0.3 mg/cm^2 attached.

[0032] <Evaluation standards>

O: No iris phenomenon due to the interference

Δ: Slight existence of the iris phenomenon due to the interference

X: Existence of the iris phenomenon due to the interference

Also, a methylene blue was attached to the optical catalyst title, and the optical catalyst effect was investigated by measuring the amount of said methylene blue decomposed. The results are shown in Table 1.

[0033] The attachment of the methylene blue and the decomposition reaction conditions are as follows.

[0034] <Methylene blue decomposition testing method> A mask having an opening part of 2 x 2 cm was placed on the tile, and 5 μL methylene blue ethanol solution with a concentration of 0.01% was dropped on it and dried. After drying, the tile was put into a lighting chamber and irradiated with lights. As a light source, a BLB lamp was used, and the amount of light being irradiated was UV intensity of 2.0 mW/cm^2 on the surface of the specimen. The residual amount of methyl blue of the tile surface was measured with time as a reflectance of a blue light by using a spectrophotometer, and the time until 1/2 of the initial amount was attained as a half life of the methylene blue.

[0035] Furthermore, for the optical catalyst tile, the adhesive strength of the coated film of the surface was evaluated by the following method.

[0036] <Method for testing the adhesive strength of coated films> In a rotational wear test according to JIS-6909, an unwoven fabric nylon brush (Scotch Bright 51 Line White made by Sumitomo 3M Ltd.) was used as an abrasive, and the polishing load was set to 1 kg/70 cm2. The polishing times for peeling-off the coated film was attained.

[0037] Comparative Examples 1 and 2

Similarly to Application Example 1 except for setting the vapor deposition chamber residence time to 30 sec in Comparative Example 1 and 10 sec in Comparative Example 2 and setting the temperature of the $TiCl_4$ vapor generating furnace 5 to 35°C, TiO_2 optical catalytic coated films with a thickness shown in Table 1 were formed and similarly evaluated. The results were shown in Table 1.

[0038] Comparative Examples 3 and 4

Similarly to Application Example 1 except setting the temperature of the heating zone to 200°C or 850°C, optical catalyst tiles were manufactured, and a similar evaluation test was carried out. The results are shown in Table 1.

[0039] Comparative Example 5

An optical catalyst tile to which TiO_2 was attached was manufactured at a ratio of 0.3 mg/cm^2 on the average on the surface of the tile by a sol-gel method instead of the CVD method, and a similar evaluation test was carried out. The results are shown in Table 1.

[0040]

(TABLE 1)

例		加熱ゾーン温度 (℃)	TiO_2 光触媒性被膜の厚み (μm)	干渉による虹彩現象の有無	メチレンブルー分解試験による半減期 (min)	被膜の剥離する研磨回数
実施例	1	650	0.85	○	10	2万回で剥離なし
	2	650	1.00	○	5	2万回で剥離なし
	3	650	1.2	○	3	2万回で剥離なし
比較例	1	400	0.6	×	180	2万回で剥離なし
	2	400	0.1	△	メチレンブルー分解認められない	2万回で剥離なし
	3	200	0.8	○	メチレンブルー分解認められない	10回で剥離
	4	850	0.9	○	180	2万回で剥離なし
	5	—	1.0	○	メチレンブルー分解認められない	1000回で剥離

/5

1. Example
2. Heating zone temperature (°C)
3. Thickness of TiO_2 optical catalytic coated film (m)
4. Existence of the iris phenomenon due to interference
5. Half life of membrane blue decomposition test (min)
6. Polishing times for peeling-off the coated film
7. Application Example
8 Comparative Example
9. No peeling-off at 20,000 times
10. Peeling-off at 10 times
11. Peeling-off at 1,000 times
12. No membrane blue decomposition can be seen.

[0041]

(Effect of the invention)

As mentioned above in detail, according to the optical catalytic tile and its manufacturing method of the present invention, an optical catalyst tile that has no iris phenomenon due to the interference, has a coated film with excellent optical catalyst performance and high adhesive strength, and is excellent in the contamination prevention and the self-cleaning action is provided.

[0042] The optical catalyst tile of the present invention can be effectively used as various kinds of interior and exterior construction materials, and its surface can be cleanly and beautifully maintained over a long term.

4. Brief description of the figure

Figure 1 is a systematic diagram for explaining the method for forming a TiO_2 vapor-deposited film by a CVD.

Explanation of numerals:

1 Tile transfer belt

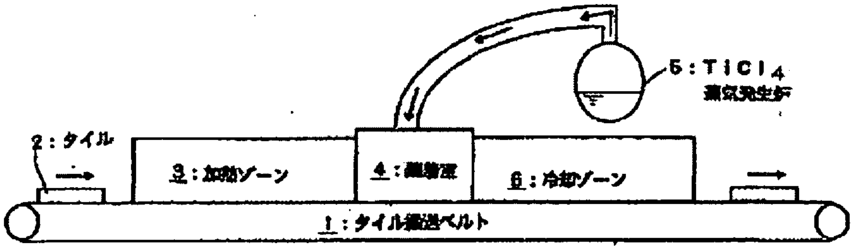
2 Tile

3 Heating zone

4 Vapor deposition chamber

5 $TiCl_4$ vapor generating furnace

6 Cooling zone



1 Tile transfer belt

2 Tile

3 Heating zone

4 Vapor deposition chamber

5 $TiCl_4$ vapor generating furnace

6 Cooling zone